

2006年 5月30日 11時09分

SONDERHOFF &amp; EINSEL

NO. 8983 P. 29/70

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Title: Method for depositing a coating material onto the surfaces of fluorescent material particles

### SPECIFICATION

Title of the Invention    Method for depositing a coating material onto the surfaces of fluorescent material particles

#### Scope of Claims for Patent

A method of depositing a coating material onto the surfaces of fluorescent material particles, the method comprising an ultrasonic wave irradiation step in a step of depositing the coating material onto the fluorescent material particles.

#### Detailed Description of the Invention:

As for the fluorescent materials of various colors that constitute the fluorescent surface of, e.g., a color cathode-ray tube; for example, green fluorescent material,  $\text{ZnCdSi} : \text{Cu}$ ,  $\text{Al}$ , a blue fluorescent material,  $\text{ZnS} : \text{Ag}$ , a red fluorescent material,  $\text{Y}_2\text{O}_3 : \text{Eu}$ , it is desirable to cover the surface thereof with a coating material such as oxides of the respective colors, phosphate or hydroxides.

2006年 5月30日 11時09分

SONDERHOFF &amp; EINSEL

NO. 8983 P. 30/70

The purpose of depositing such coating materials is for improving the dispersion of the fluorescent material particles or for preventing the fluorescent material particles from being contaminated by the impurities or for preventing the deterioration in the characteristics and the brightness of the fluorescent materials due to the baking treatment performed after applying this kind of fluorescent materials onto the inner surface of the panel in the cathode-ray tube, respectively.

In case of depositing the coating material onto the surfaces of such fluorescent particles, it is very important in improving the performance of the fluorescent surface that the deposition of the coating material is made uniformly.

However, in actuality, the ordinary method of depositing the coating material has the drawback that, when the treatment for deposition of the coating material is performed, the fluorescent material particles are damaged or crosslinking is caused between the particles by the coating material to form aggregates of particles, which lowers the brightness.

The present invention is intended to provide a method of depositing a coating material onto the surfaces of the fluorescent material particles, according to which method the above-mentioned drawback is eliminated; and the surfaces of the fluorescent material particles can be coated with the coating material uniformly and without fail.

2006年 5月30日 11:09分

SONDERHOFF &amp; EINSEL

NO. 8983 P. 31/70

More specifically, according to the present invention, an ultrasonic wave irradiation step is provided among the steps of depositing the coating material onto the fluorescent material particles.

Further, it has been confirmed that, in case such an ultrasonic wave irradiation is carried out, the fluorescent material particles are separated and dispersed without being crushed or damaged by the ultrasonic wave irradiation and thus loosened into a single-particle state, and the surfaces of these particles is uniformly coated with the coating material.

An embodiment of the present invention will now be described, referring to Fig. 1. According to the present invention, there is prepared a suspension made in such a manner that the fluorescent material particles the surfaces of which are to be coated with the coating material are suspended into pure water at a concentration of 1 to 30 g/100 cc, and the thus prepared suspension is put into a cell 1 for ultrasonic wave irradiation. Then, onto this suspension, ultrasonic waves with a frequency of 20 to 100 KHz are irradiated. The reference numeral 2 denotes an ultrasonic wave generation means, and numeral 3 denotes a vibrator, which is coupled to the cell 1.

On the other hand, a coating material such as, e.g., colloidal silica which is to be deposited onto the above-mentioned fluorescent material is put into a cell 4 similarly for ultrasonic wave irradiation, in which

2006年 5月30日 11時10分

SONDERHOFF &amp; EINSEL

NO. 8983 P. 32/70

ultrasonic waves with a frequency of 50 KHz to 10 MHz are irradiated. Numeral 5 denotes an ultrasonic wave generation means for generating said ultrasonic wave, and numeral 6 denotes a vibrator therefor, which is coupled to the cell 4.

The fluorescent material suspension in which the fluorescent material particles were dispersed in the cell 1 and the colloidal silica in which the colloid particles were dispersed in the cell 4 are fed to an agitator 7, so that, by this agitator 7, agitation is performed to deposit the silica onto the surfaces of the fluorescent material particles.

The suspension of fluorescent material particles with their surfaces coated with silica in the above-described manner is then put in a cell 8 for ultrasonic wave irradiation, where ultrasonic wave irradiation is performed at a frequency 20 to 300 KHz for dispersion. Reference numeral 9 denotes an ultrasonic wave generation means, and reference numeral 10 denotes a vibrator, which is coupled to the cell 8.

In this cell 8, the fluorescent material particles are well dispersed to be made to single particles. With this, each particle is uniformly coated with the coating material. The fluorescent material particles thus dispersed and coated with the coating material are fed to a dryer 11, wherein a drying process is performed.

2006年 5月30日 11时10分

SONDERHOFF &amp; EINSEL

NO. 8983 P. 33/70

Next, an example of the ultrasonic wave irradiation cells 1 and 4 is described with reference to Fig. 2.

This cell has a longitudinal container 50, which is provided at its lower end portion with a supply port 51 that supplies a suspension to be subjected to ultrasonic wave irradiation and dispersion. The container 50 is provided at an appropriate upper position with a takeout port 52 for the suspension. In this case, as shown in dotted lines, a plurality of takeout ports 52 can be provided at desired intervals in a longitudinal direction of the container 50, thereby allowing the suspension to be taken out from one of the takeout ports 52 that is selected.

The container 50 is provided at its lower end with a discharge port 53. Also, the container 50 has coupled, for example, to its lower end, the vibrator 3 of the ultrasonic wave generation means 2 or the vibrator 6 of the ultrasonic wave generation means 5. Furthermore, the container 50 is provided outside thereof with an outer box 54 having a lower end provided with a cooling water supply port 55, from which cooling water is fed and is then discharged from a discharge port 56 provided at an upper end.

Now, in the above-described structure, a suspension of a desired flow amount to be dispersed is fed from the supply port to the container 50 for ultrasonic wave irradiation. With this, fluorescent material particles in the suspension are separated to single particles, thereby decreasing their particle size and, as being dispersed,

they move up with the flow of a liquid forming the suspension through the container 50 to each of the upper takeout ports. In this case, a residence time of the particles in the container 50 is longer as the particle size of the particles is larger. A reason for this is as follows. If the particle size of the particles is small, a settling rate in the liquid is nearly negligible. Therefore, these particles go up with the flow of the liquid to the upper portion of the container 50 at a rate determined by a flow rate of this liquid. Thus, the suspension of the particles with such a small particle size is taken out from the upper takeout port 52. If the particle size of the particles is large, its settling rate is fast, and therefore a rate at which such particles go up to the upper portion of the container 50 is slower than the flow rate of the liquid. After all, a substantial residence time in this container 50 is long. In other words, particles with a larger particle size are subjected to ultrasonic wave irradiation for a longer time, and their separation and dispersion are more effectively performed. After all, a suspension with particles having an almost uniform particle size being dispersed can be obtained from the upper portion of the container 50. Then, a suspension with particles having a larger particle size is taken out from a lower takeout port 52.

Therefore, when the above-structured cells 1 and 4 are used to perform ultrasonic wave irradiation on a

2006年 5月30日 11时11分

SONDERHOFF &amp; EINSEL

NO. 8983 P. 35/70

fluorescent material suspension and a suspension of the coating material, the respective particles can be reliably separated and dispersed.

Also, the cell 8 can have a structure similar to that described with reference to Fig. 2. In this case, the coating material is deposited as ultrasonic wave irradiation proceeds during passage through the container 50.

The fluorescent material particles dried by the dryer 11 and then taken out therefrom in the manner described above are such, as shown in Fig. 3 depicting a sketch based on a microphotograph of 3600 times power, that the surface of a fluorescent material particle 12 is uniformly deposited with a coating material 13, and also the respective particles are well dispersed as single particles.

Fig. 4 is a sketch of a microphotograph of similarly 3600 times power depicting a fluorescent material particle according to the conventional method with the coating material being deposited without an ultrasonic wave irradiation process. In this case, although the surface of the fluorescent material particle 12 is deposited with the coating material 13, as shown in a portion 13a, coating is non-uniform with a concentration of the coating material. Moreover, with this coating material 13, as shown in a portion 13b, a plurality of fluorescent material particles are mutually cross-linked and agglomerated.

2006年 5月30日 11时11分

SONDERHOFF &amp; EINSEL

NO. 8983 P. 36/70

As described above, according to the method of the present invention, in the process of depositing the coating material onto the surfaces of the fluorescent material particles, ultrasonic wave irradiation is performed, thereby allowing the fluorescent material particles to be separated in an approximately uniform single-particle state and to be well dispersed. Also on the surfaces of the fluorescent materials, the coating material can be uniformly applied. Thus, when such a fluorescent material is used to form a color fluorescent surface of a cathode-ray tube, a fluorescent surface with a uniform high brightness can be obtained.

Here, the above-described example is the case where the fluorescent material powder and the coating material are each subjected to ultrasonic wave irradiation in the cells 1 and 4. In some cases, these can be omitted.

Also, the above-described example is the case where a process of coating the coating material is performed by two processes, that is, agitation by the agitator 7 and ultrasonic wave irradiation by the cell 8. Alternatively, these can be performed simultaneously. However, for example, when the coating material is deposited onto the surface of the fluorescent material through electrical connection, in some cases, deposition may be performed better when the coating is deposited first only through agitation without provision of ultrasonic wave vibration. In such cases, as described with reference to Fig. 1, a



2006年 5月30日 11時11分

SONDERHOFF &amp; EINSEL

NO. 8983 P. 37/70

process of agitating the fluorescent material particles and the coating material and a process of ultrasonic wave irradiation are preferably performed separately in sequence.

Here, to obtain a color fluorescent surface by applying fluorescent material particles coated with the coating material in the manner described above to a panel inner surface of the cathode-ray tube, fluorescent material slurries of respective colors are prepared, each of which is obtained by mixing a fluorescent material of each color with a photosensitizing liquid composed of a photosensitizing agent, for example, polyvinyl alcohol and dichromate ammonium. A fluorescent material slurry of one of the colors is applied to the inner surface of the panel, is optically burnt into a predetermined pattern, and then is subjected to a developing process to remove a portion not exposed or hardened, thereby obtaining a predetermined fluorescent material pattern. Such a process is performed for the fluorescent material of each color, thereby normally obtaining a color fluorescent surface with fluorescent material patterns of respective colors being applied.

As described above, to obtain a color fluorescent surface, a fluorescent material slurry is formed by mixing a fluorescent material and a photosensitizing liquid and, by using this slurry, a fluorescent surface is formed. In this case, as a device for obtaining such a fluorescent material slurry, it is preferable to use a fluorescent

material slurry manufacturing device having a special structure.

That is, in general, to obtain this fluorescent material slurry, a fluorescent material and a photosensitizing liquid are mixed in a ball mill for a long time so that they are well dispersed. However, when the fluorescent material and the photosensitizing liquid are mixed and agitated in this manner, attrition and damages occur at the fluorescent material particles, thereby disadvantageously decreasing their brightness.

Moreover, an effective application thickness and a particle size distribution of the fluorescent material with respect to the inner surface of the panel of the cathode-ray tube are important in determining its brightness, uniformity of brightness, and hues. Also, predominant factors for these effective application thickness and particle size distribution of the fluorescent material are the viscosity of the fluorescent material slurry and a distribution state of the fluorescent material particles.

The special fluorescent material slurry manufacturing device described above is configured so as to be able to obtain a fluorescent material slurry in which a fluorescent material is well dispersed in a photosensitizing liquid without attrition or damages on the fluorescent material, and also to be able to automatically control the viscosity of the fluorescent material slurry and the particle size of

2006年 5月30日 11時12分

SONDERHOFF &amp; EINSEL

NO. 8983 P. 39/70

the fluorescent material particles therein respectively as desired.

That is, in the specially-configured fluorescent material slurry manufacturing device, when a photosensitive resin of a photosensitizing liquid forming a fluorescent material slurry, for example, a liquid mixture of polyvinyl alcohol and dichromate ammonium, is subjected to ultrasonic wave irradiation, a depolymerization action occurs to decrease the viscosity. Also, when ultrasonic wave irradiation is performed on the fluorescent material particles, their dispersion is effectively performed. By using these facts, ultrasonic wave irradiation is performed on at least the fluorescent material slurry. Then, the finally-obtained viscosity of the fluorescent material slurry and particle size of its fluorescent material particles are detected. Then, based on the detection signals, adjustment of the viscosity and the particle size is controlled.

Here, a relation between an irradiation time of irradiating the fluorescent material slurry with ultrasonic waves and the viscosity of the slurry is as shown in Fig. 5. Therefore, when the viscosity of the slurry is selected to be 180 Cp, for example, its ultrasonic wave irradiation time is selected to be 4 minutes.

With reference to Fig. 6, this specially-configured fluorescent material slurry manufacturing device is described.

2006年 5月30日 11时12分

SONDERHOFF &amp; EINSEL

NO. 8983 P. 40/70

This device is configured to have a particle size adjusting means 20 for fluorescent material powder, a viscosity adjusting means 21 for a photosensitizing liquid, a means 22 of irradiating a fluorescent material slurry formed of a liquid mixture of the photosensitizing liquid and the fluorescent material with ultrasonic waves, a means 23 of detecting a viscosity of the fluorescent material slurry extracted from the means 22, and a means 24 of detecting a particle size. Based on a detection signal extracted from the detecting means 23, the ultrasonic wave irradiating means 22 for the fluorescent material slurry is controlled for the purpose of viscosity adjustment, and also the viscosity adjusting means 21 for the photosensitizing liquid is controlled. Also, based on a detection signal from the particle size detecting means 24, the particle size adjusting means 20 is controlled.

The particle size adjusting means 20 has accommodated therein, for example, a suspension formed of fluorescent material particles, pure water, methyl alcohol, and a fluid dispersion, and is configured to have a cell 25 for ultrasonic wave irradiation for ultrasonic wave irradiation. Reference numeral 26 denotes a ultrasonic wave generation means, reference numeral 27 denotes a vibrator, which is coupled to that cell 25. In this cell 25, ultrasonic wave irradiation is performed to loosen fluorescent material particles. Then, a suspension with a substantial particle size approximately as desired is subjected to adjustment of

the fluorescent material particles by a pump 28, and then is fed to a so-called cyclone 29 for sizing based on the particle size. This cyclone 29 sizes the fluorescent material particles based on their particle sizes. For example, particles loosened to single particles with a desired fineness are fed to the means 22 of obtaining a fluorescent material slurry as shown by a passage a, whilst coarse particles are fed to another agitator container 30 as shown by a passage b. Also, at the next stage of this container 30 is a dispersing device, that is, an ultrasonic wave irradiation cell 31. Then, the suspension of the fluorescent material particles loosened by this cell 31 to have a desired particle size and dispersed is fed to the means 22. Reference numeral 43 denotes an ultrasonic wave generation means for the cell 31, and reference numeral 44 denotes a vibrator, which is coupled to that cell 31.

As a photosensitizing liquid, for example, a photosensitive resin obtained by mixing polyvinyl alcohol and dichromate ammonium described above is used. The viscosity adjusting means 21 for this photosensitizing liquid is formed of a cell 32 for performing ultrasonic wave irradiation on this liquid. Reference numeral 33 denotes an ultrasonic wave generation means, and reference numeral 34 denotes a vibrator, which is coupled to that cell 32. The photosensitizing liquid whose viscosity is made to be an approximately desired one in the cell 32 for

2006年 5月30日 11:13分

SONDERHOFF &amp; EINSEL

NO. 8983 P. 42/70

viscosity adjustment is fed by the pump 35 to the fluorescent material slurry obtaining means 22.

The fluorescent material slurry obtaining means 22 has a container 36 for accommodation and agitation of the fluorescent material and the photosensitizing liquid fed by the means 20 and the means 21. A liquid mixture of the photosensitizing liquid and the fluorescent material mixed therein is fed by a pump 37 to a cell 38 for ultrasonic wave irradiation. Reference numeral 39 denotes an ultrasonic wave generation means, and reference numeral 40 denotes a vibrator, which is coupled to the cell 38. A fluorescent material slurry obtained with the fluorescent material being dispersed in the photosensitizing liquid in the cell 38 is fed by a pump 41 to a container 42 for injecting this fluorescent material slurry to the inner surface of a cathode-ray tube panel, for example.

Then, the viscosity of the fluorescent material slurry finally obtained in the above-described manner is detected by the detecting means 23, and also its particle size is detected by the particle size detecting means 24. Then, based on a signal detected by this means 23, the viscosity adjusting means 21 for the photosensitizing liquid is controlled. For example, the viscosity is adjusted by controlling the ultrasonic wave generation means 33 of the cell 32 to select its irradiation time.

On another hand, together with the above, based on the signal detected by this viscosity detecting means 23, the

2006年 5月30日 11时13分

SONDERHOFF &amp; EINSEL

NO. 8983 P. 43/70

ultrasonic wave irradiation cell 38 for the fluorescent material slurry is controlled. For example, by controlling its ultrasonic wave generation means 39, its irradiation time, for example, is adjusted. Also, on another hand, a detection signal detected by the particle size detecting means 24 is supplied to the particle size adjusting means 20 for the fluorescent material for control. For example, the ultrasonic wave generation means 26 of the cell 25 is controlled to control its irradiation time, thereby obtaining a desired particle size.

Here, each of the cells 25, 31, 32, and 38 can have a structure similar to that of the cell described with reference to Fig. 2. In this case, the cells 32, 38, and 25 controlled by the detection signal of the detecting means 23 and 24 each perform ultrasonic wave oscillation, that is, intermittent irradiation. An oscillation time or an intermission time is controlled by the above detection signal to control a substantial irradiation time.

Here, in the cell 38, although the particle size of the fluorescent material is changed through irradiation of ultrasonic waves, practically speaking, the fluorescent material particles are in an almost single-particle state herein, and therefore irradiation of ultrasonic waves hardly has an influence on the particle size herein.

According to the above-structured fluorescent material slurry manufacturing device, the viscosity of the slurry and the particle size of the fluorescent material

2006年 5月30日 11時14分

SONDERHOFF &amp; EINSEL

NO. 8983 P. 44/70

immediately before application onto the cathode-ray tube panel are detected, thereby controlling the detected elements. Therefore, a fluorescent material slurry with desired viscosity and particle size can be reliably obtained. Furthermore, the thickness of application of the fluorescent material to the panel can be reliably selected as desired, thereby achieving uniformity of particle size distribution.

Also, attrition and damages of the fluorescent material can be prevented, thereby allowing a fluorescent surface with a large brightness to be obtained.

Still further, the fluorescent material slurry obtained in the above-described manner is applied onto the inner surface of the panel of the cathode-ray tube in the manner as described above, exposure is performed according to a desired fluorescent material pattern, and then development is performed. This application is preferably performed with the fluorescent material having a large filling density. To this end, when the fluorescent material slurry is applied to the inner surface of the panel, it is preferable that mechanical vibration or ultrasonic wave vibration be provided or the fluorescent material particles be attached by a centrifugal force so as to be pressed toward the inner surface of the panel.

For example, as shown in Fig. 7, a support 60 is provided, and on the support 60 is a container 62 formed of metal or resin or the like for accommodating a liquid



2006 5月30日 11:14

SONDERHOFF &amp; EINSEL

NO. 8983 P. 45/70

having a buffer effect, such as water 61. To the container 62, a vibrator 64 of the ultrasonic wave generation means 68 is coupled. Also, in the buffer solution 51, a cathode-ray tube panel 65 to which the fluorescent material slurry is to be applied is placed with its internal surface upward, and a fluorescent material slurry 66 is poured to the internal surface of the panel. In such a state, ultrasonic wave vibrations are provided by the ultrasonic wave generation means 63. The frequency of the ultrasonic waves in this case is selected to be, for example, 20 KHz to 2 MHz. Here, a reason for setting the frequency not higher than 2 MHz is that, if the frequency is too high, the fluorescent material particles will be again agglomerated. Furthermore, a peak-to-peak vibration width of the vibrations can be selected to 10 to 80 microns.

Alternatively, as shown in Fig. 8, with provision of mechanical vibrations, the fluorescent material slurry 66 can be applied to the inner surface of the panel 65. In this case, a buffer 68, such as resin, having a desired elasticity is provided on a support 67, and the panel 65 is placed on the buffer 68, with its upper surface upward. Then, the slurry 66 is poured to the inner surface of the panel 65. In such a state, mechanical vibrations are provided by a mechanical vibration generation means 69 for reciprocating vibrations of the panel 6 in a horizontal or vertical direction. In this case, with the number of

2006年 5月30日 11時14分

SONDERHOFF &amp; EINSEL

NO. 8983 P. 46/70

vibrations being 1000 to 1800/minute, its vibration width can be selected to be on the order of 20 to 1000 microns.

Still alternatively, a panel rotating device 70 is provided capable of holding the panel 65 as shown in Fig. 9 and rotating it around a shaft center 0-0. Reference numeral 71 denotes a rotating shaft of the device 70 capable of rotating around the axis 0-0. The panel 65 is set so that the inner surface of the panel faces the axis 71 side by a holder 72 mounted on the rotating shaft. With the slurry 66 being applied to the inner surface of the panel 65, it is rotated around the shaft center 0-0 at a rotation speed of, for example, 500 rpm.

In this manner, when the florescent material slurry 66 is applied through mechanical vibrations, ultrasonic wave vibrations, or a centrifugal force, the filling density of the fluorescent material particles can be increased. Therefore, "blur" or "covering" that would occur when the florescent materials are sequentially applied can be avoided. That is, when the fluorescent material can be applied with a high filling density, since the filling density of a fluorescent material previously applied is large, a fluorescent material of a fluorescent material slurry to be applied next is prevented from being infiltrated into the above. Therefore, when it is developed, the next fluorescent material on the previously-applied fluorescent material can be reliably removed.

2006年 5月30日 11時15分

SONDERHOFF &amp; EINSEL

NO. 8983 P. 47/70

As described above, the fluorescent material powder is made into a fluorescent material slurry, which is applied to the inner surface of the panel to form a color fluorescent surface. When using a fluorescent material obtained by uniformly applying a coating material on the surfaces of the fluorescent material particles through the method according to the present invention described above, dispersion of the fluorescent material can be effectively performed, and also the fluorescent material can be protected against fracture at the time of dispersion. Also, protection against impurities can be reliably performed. In addition to that, a decrease in brightness after application to the panel of the cathode-ray tube and then burning in the following process can be reliably prevented. Thus, the present invention has a significant advantage in practice.

#### Brief Description of the Drawings

Fig. 1 is a structural diagram showing one example of device implementing the method of the present invention; Fig. 2 is a section view of an ultrasonic wave irradiation cell; Fig. 3 is a sketch of a microphotograph of a fluorescent material particle obtained through the method of the present invention; Fig. 4 is a sketch of a microphotograph of a fluorescent material particle in the case of the conventional method; Fig. 5 is a curve chart depicting a relation between an ultrasonic wave irradiation time and viscosity with respect to a fluorescent material

2006年 5月30日 11时15分

SONDERHOFF &amp; EISEL

NO. 8983 P. 48/70

slurry; Fig. 6 is a schematic structural diagram of one example of a device for obtaining the fluorescent material slurry; and Figs. 7 to 9 are schematic layout drawings that each depict a means of depositing the fluorescent material slurry onto a cathode-ray tube panel.

Reference numerals 1, 4, and 8 each denote an ultrasonic wave irradiation cell, reference numeral 7 denotes an agitator, reference numeral 11 denotes a dryer, reference numeral 12 denotes a fluorescent material particle, and reference numeral 13 is a coating material.

Applicant for Patent

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2006年 5月30日 11時15分

SONDERHOFF & EINSEL

NO. 8983 P. 49/70

Fig. 5

501 VISCOSITY (CP)

502 IRRADIATION TIME (MINUTE)

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